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(54) Title: METHOD FOR TREATMENT OF SILICON DIOXIDE CONTAINING MATERIAL

(57) Abstract

The present invention relates to a method for treatment of silicon dioxide containing materials showing a pozzolanic activity. The silicon dioxide containing materials are subjected to a heat treatment at a temperature of at least 500 °C whereafter the silicon dioxide containing materials are subjected to milling for a time period necessary to recover the pozzolanic activity of the materials.

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Title: Method for treatment of silicon dioxide containing material.

Technical Field

The present invention relates to a method for the treatment of substantially amorphous silicon dioxide containing materials having pozzolanic activity, and more particularly to the treatment of microsilica recovered from off gases which evolve during production of silicon and ferrosilicon and fly ash recovered when burning coal in coal fired power plants.

Background Art

Microsilica which is recovered from off gases from smelting furnaces for the production of silicon and ferrosilicon has a strong pozzolanic activity and has for this reason been used as an additive in mortar and concrete. Microsilica has a small particle size of less than 0.5 μm and a surface area between 10 and 30 m^2/gram. The colour of microsilica varies between black and light grey, the colour being mainly dependent on the content of carbon in the individual particles. The dark and very often uneven colour makes microsilica unusable for a number of applications where a white colour is required.

From US patent No. 5,290,529 it is known to subject microsilica to a heat treatment at a temperature in the range between 550°C to 750°C in order to combust carbon in the particles whereby a white microsilica is obtained. This known heat treatment of microsilica unfortunately has the drawback that the pozzolanic activity of microsilica is lost. The value of microsilica as an additive for concrete and morter is thereby substantially reduced.

Also, fly ash produced during the firing of coal in coal fired power plants shows pozzolanic activity. Fly ash contains a substantial amount of amorphous SiO_2 and has a particle size between 1 and 100 μm. The colour of fly ash is, however, black or dark grey and fly ash can therefore not be used as an additive in concrete and mortar where a white colour is required. Also,

fly ash can be made white by heat treatment. However in the same way as for microsilica it has been found that the pozzolanic activity of fly ash is lost during heat treatment.

Disclosure of Invention

It is an object of the present invention to provide a method for the treatment of silicon dioxide containing material whereby the silicon dioxide containing materials are heat treated and where the pozzolanic effect of the material are restored after the heat treatment.

Accordingly the present invention relates to a method for the treatment of silicon dioxide containing materials showing a pozzolanic activity, where the silicon dioxide containing materials are subjected to a heat treatment at a temperature of at least 500°C whereafter the silicon dioxide containing materials are subjected to milling for a time period necessary to recover the pozzolanic activity of the materials.

The heat treated silicon dioxide containing materials are subject to milling for a time period of at least 30 minutes and preferably for a time period of at least 60 minutes.

It was surprisingly found that the pozzolanic activity of these materials could be restored by subjecting the heat treated materials to a milling process. In some cases it was even found that an increased pozzolanic activity was achieved compared to the pozzolanic activity of the untreated material. The milling of the heat treated materials can be carried out both by dry milling or by wet milling. Dry milling can be carried out by the use of known methods such as ball mills and rod mills of different kinds, colloid mills and fluid energy mills. Wet milling can also be carried out in ball mills, rod mills, colloid mills and in fluid energy mills.

As microsilica for use as an additive for concrete and mortar often is supplied as aqueous slurries, it is in such cases especially preferred to carry out the milling as wet milling.

A further advantage of the method according to the present invention is that the heat treatment can be carried out at higher temperatures than is used in the known processes for heat treatment of microsilica. The reason for this is that sintering of particles which to some extent will take place during heat treatment at high temperatures, will be broken down during the subsequent milling process and thus not give agglomerates in the final product.

Detailed description of preferred embodiment

The present invention will now be further described by way of examples.

Example 1

Microsilica from Elkem ASA was heat treated at different temperatures and for different time intervals. The heat treatment was carried out by placing microsilica in a porcelain crucible which was put into a muffle furnace and heated at the temperatures and time periods as stated in Table 1.

A part of the heat treated microsilica was mixed with water to form a slurry and thereafter milled in a laboratory wet mill, Model 12, delivered by Boulton, England.

The pozzolanic activity of untreated microsilica, heat treated microsilica and heat treated and wetmilled microsilica was investigated by casting prisms of mortar and measuring the pressure strength of the prisms after curing of the mortar. The composition of the mortars was the same for all the tests. The composition of the mortar was as follows: 20 % by weight of cement, 2.2 % by weight of microsilica, 11.1 % by weight of water and 66.7 % by weight of sand (DIN EN 196-1).

For comparison purposes, a mortar was also produced which did not contain microsilica.

The results are shown in Table 1.

TABLE 1

Microsilica sample No.	Heat treatment		Milling, hours	Whiteness* %	Pressure strength after 28 days at 20 ^0C, MPa
	Temp ^0C	Time, hours			
B1	none	-	none	18.9	60.8
B2	750	2	none	61.8	53.3
B3	750	2	1 hour	61.8	63.9
B4	750	2	2 hour	61.8	67.6
None	-	-			50.5

* Measured by a method where black felt has a whiteness of zero and where $BaSO_4$ has a whiteness of 98.6.

The results in Table 1 show that the whiteness of microsilica after heat treatment as expected increased substantially, but that the pozzolanic activity was completely lost as the pressure strength of the mortar produced from sample B2 was reduced to about the same as for the mortar containing no microsilica. Table 1 further shows that the pozzolanic activity was at least restored by the wet milling as the pressure strength after milling for 1 hour (sample B3) was higher than for the untreated microsilica (sample B1) and the pressure strength after milling for 2 hours (sample B4) was substantially higher than for the mortar produced by addition of untreated microsilica.

Example 2

Another sample of microsilica from Elkem ASA was heat treated in the same way as described in Example 1. The temperatures and the heat treatment times are stated in Table 2. Samples of the heat treated microsilica were

subjected to wet milling for different time periods in the same manner as described in Example 2.

The pozzolanic activity for untreated microsilica, heat treated microsilica and for heat treated and wet milled microsilica was investigated by casting prisms of mortar and testing the pressure strength of the prisms. The composition of the mortars was the same as in Example 1. For comparison purposes, a mortar was also produced without microsilica.

The results are shown in Table 2.

TABLE 2

Microsilica Sample No.	Heat treatment		Milling time, hours	Whiteness* %	Pressure strength of mortar after 28 days at 20^0C, MPa
	Temp ^0C	Time, hours			
C1	none	-	none	33.4	61.0
C2	750	2	none	59.5	59.3
C3	750	2	2 hours	59.5	67.6
C4	750	2	13 hours	59.5	67.6
none	-	-			50.5

* Measured by a method where black felt has a whiteness of zero and where $BaSO_4$ has a whiteness of 98.6.

The results in Table 2 show that the whiteness of microsilica after heat treatment as expected was substantially increased, but that the pozzolanic activity was reduced as the pressure strength of the mortar produced with sample C2 was reduced compared to the mortar produced with untreated microsilica (sample C1). Table 2 further shows that the pozzolanic activity of microsilica strongly increased during the wet milling as the pressure strength after milling for 2 hours (sample C3) was better than for the untreated microsilica (sample C1). Finally, the results in Table 2 shows that wet milling

for more than 2 hours (sample C4) does not show any further increase in the pozzolanic activity for the microsilica.

Example 3

A third sample of microsilica from Elkem ASA was heat treated in the same way as described in Example 1. A sample of the heat treated microsilica was subjected to dry milling in a jet mill to a nominal particle size of 10 μm. The pozzolanic activity for untreated microsilica, heat treated microsilica and heat treated and dry milled microsilica was investigated by casting prisms of mortars and measuring the pressure strength of the mortars. The composition of the mortars was the same as described in Example 1.

The results are shown in Table 3.

TABLE 3

Microsilica Sample No.	Heat treatment		Milling in jet mill	Whiteness* %	Pressure strength of mortar after 28 days at 20^0C, MPa
	Temp ^0C	Time, hours			
E1	none	-	no	66.8	61.0
E2	750	2	no	73.0	46.6
E3	750	2	yes	89.0	58.4

* Measured by a method where black felt has a whiteness of zero and where $BaSO_4$ has a whiteness of 98.6.

The results in Table 3 show that the whiteness of microsilica after heat treatment increased even if the whiteness of the untreated microsilica (sample E1) was high. The pozzolanic activity was strongly reduced by the heat treatment. Table 3 shows that by dry milling of the heat treated microsilica in jet mill (sample E3), a pressure strength of the mortar was obtained which was about the same as the pressure strength for the mortar containing untreated microsilica (sample E1). This shows that the pozzolanic

activity was substantially recovered by the method according to the present invention. Table 3 further shows that by dry milling of the heat treated microsilica, a surprising increase in the whiteness of the microsilica was obtained compared to the whiteness of the heat treated microsilica.

CLAIMS

1. A method for the treatment of silicon dioxide containing materials showing a pozzolanic activity, which comprises subjecting the silicon dioxide containing materials are to a heat treatment at a temperature of at least 500°C, c h a r a c t e r i z e d by subjecting the silicon dioxide containing materials, after the heat treatment, to milling.

2. A method according to claim 1, c h a r a c t e r i z e d by subjecting the silicon dioxide containing materials to milling for a time period of at least 30 minutes.

3. A method according to claim 2, c h a r a c t e r i z e d by subjecting the silicon dioxide containing materials to milling for a time period of at least 60 minutes.

4. A method according to claim 1 - 3, c h a r a c t e r i z e d i n that the heat treated materials are subjected to wet milling.

5. A method according to claim 1 - 3, c h a r a c t e r i z e d i n that the heat treated materials are subjected to dry milling.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/NO 97/00088

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C04B 18/08, C04B 18/14 // C04B 7/26
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

DIALOG: WPI, CLAIMS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Patent Abstracts of Japan, Vol 14,No 290, C-731, abstract of JP,A,2-92851 (MITSUBISHI HEAVY IND LTD), 3 April 1990 (03.04.90) --	1-5
A	Patent Abstracts of Japan,, abstract of JP,A, 3-137041 (MITSUBISHI MATERIALS CORP), 11 June 1991 (11.06.91) --	1-5
A	WO 9527685 A1 (N.V. KEMA), 19 October 1995 (19.10.95), page 3, line 25 - line 27 -- --------	1-5

☐ Further documents are listed in the continuation of Box C.   ☒ See patent family annex.

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Information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9527685 A1	19/10/95	CA 2186248 A	19/10/95
		EP 0758308 A	19/02/97
		NL 9400564 A	01/11/95